Minicolloque n° CPR2 **X Oral** **☐ Poster**

Nano-ions in soft matter – From chaotropic to hydrophobic ions

Max Hohenschutz[a,b*], Olivier Diat[a] and Pierre Bauduin[a]

a. ICSM, CEA, CNRS, ENSCM, Univ. Montpellier, Marcoule, France
b. Institute of Physical Chemistry, RWTH Aachen University, 52056 Aachen, Germany
* email : hohenschutz@pc.rwth-aachen.de

Nanometer-sized multiatomic species, such as polyoxometalates and boron clusters, have attracted much attention in recent years due to their fascinating solution behavior. Baring much lower charge densities than classical ions, such as Cl^- or SCN^-, these so-called nano-ions show a strong propensity to adsorb to non-ionic surfaces (e.g. on non-ionic surfactant micelles[1]) or to self-assemble in bare water (e.g. vesicle and micelle formation for COSAN[2]). These phenomena arise due to a strong chaotropic (or superchaotropic) driving force, which results from a enthalpically favorable water-structure recovery in the bulk as the nano-ion self-assembles or adsorbs to an interface.[3] Nano-ions thus act as surfactant but without the classical hydrophilic-hydrophobic structural motifs and constitute promising novel constituents for soft matter formulations.[4] In this contribution, we give an overview over recent developments in nano-ion related research, and additionally propose a classification of the typically investigated nano-ions spanning from chaotropic over superchaotropic to hydrophobic. To this end, we investigate the phase behavior of the ethoxylated non-ionic surfactant C_8E_4 as a function of nano-ion type and concentration and characterize it using SANS and SAXS. We find that the micellar phase is increasingly stabilized to higher temperatures for the nano-ions with lower charge densities, see the increase in the characteristic cloud point temperature of the C_8E_4-micellar phase in Fig.1a. Additionally, for the lowest charge density nano-ions, such as $COSAN^-$, see Fig.1b, the cloud point increased even more strongly and a vesicle phase emerged at higher temperatures, while at high nano-ion concentrations the C_8E_4-micellar phase precipitated indicating a disruptive or hydrophobic behavior of $COSAN^-$. With decreasing charge densities, the nano-ions hence range from chaotropic to superchaotropic to hydrophobic as an extension to the classical Hofmeister series.

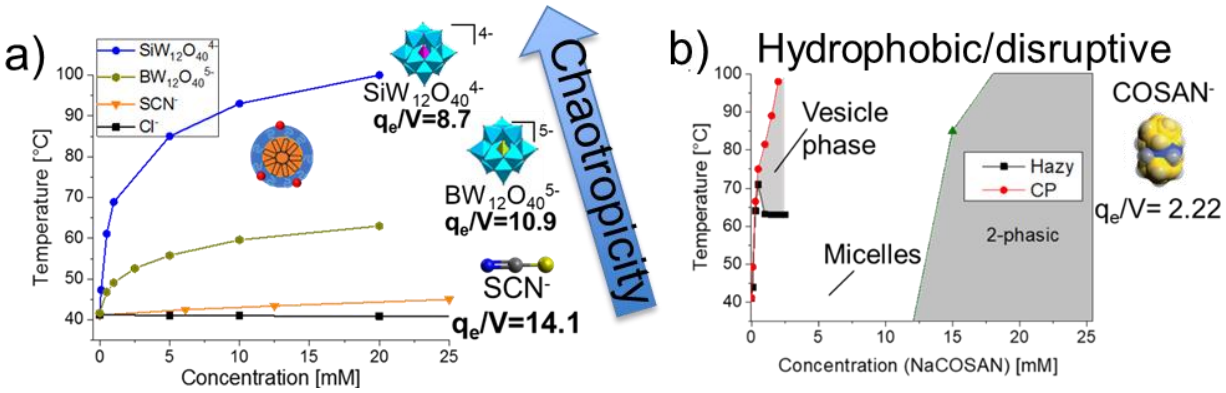

Figure 1: Phase behavior of 60 mM C_8E_4 in the presence of nano-ions with charge densities q_e/V in nm^{-3}: a) Cloud point evolution as a function of the concentration of NaCl, NaSCN, $K_5BW_{12}O_{40}$ and $SiW_{12}O_{40}^{4-}$. b) Phase diagram as a function of NaCOSAN-concentration with a vesicle phase and a 2-phasic region.

1. Naskar et al. J. Phys. Chem. C 2015, 119 (36), 20985-20992.
2. Bauduin et al. Angew. Chem. Int. Ed. 2011, 50 (23), 5298-5300.
3. Assaf et al. Ang. Chem. Int. Ed. 2018, 57 (43), 13968-13981.
4. Hohenschutz et al. Angew. Chem. Int. Ed. 2020, 59 (21), 8084-8088.